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Laser microprobe

In a laser microprobe with a pulsed laser for excitation of samples (1) and with a transit time mass spectrometer (4, 5) which comprises path (4) an electrode system (9) which is used to shape an ion pulse defined in time from the plasma which is formed by excitation of sample (1) precedes transit time path (4) (Figure 1).

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### Laser microprobe

The invention relates to a laser microprobe with a pulsed laser for excitation of a sample and with a transit time mass spectrometer which comprises a path.

Laser microprobes of this type have been known (compare Nature, Vol. 256, July 10, 1975) and commercially available for a long time. Use of a transit time mass spectrometer as a mass analyzer has proven especially advantageous since the prerequisite of the presence of ion pulses which is necessary for a transit time mass spectrometer as a result of pulsed sample excitation is satisfied. The use of the advantages of transit time mass spectrometry (sensitive, results quickly available over the entire mass range) was therefore easily possible.

With respect to resolution, the measurement results however do not always meet expectations. Line broadening which makes it difficult to recognize nearby masses occurred especially in the analysis of solid samples (nontransparent, preferably inorganic samples).

Therefore the object of this invention is to devise a laser microprobe of the initially mentioned type with resolution which is easily improved.

According to the invention this object is achieved by the fact that the transit time path of the transit time mass spectrometer is preceded by an electrode system for shaping an

ion pulse defined in time from the plasma which is formed by excitation of the sample. This invention is based on the recognition that even in the shortest laser pulses in the ps range, especially in the excitation of solid surfaces, the ion plasma generated by the laser pulse in the area of the sample surface is present for much longer than can be expected according to the duration of the laser pulse. There is therefore no defined starting time for the ions to be analyzed in spite of short laser pulses. Using the electrode system according to the invention it is now possible to shape an ion pulse defined in time from the plasma which is formed by laser excitation and to feed it to the transit time mass spectrometer. Smearing as a result of the plasma which exists for a longer time no longer occurs, by which resolution is greatly improved.

Other advantages and details will be explained using Figures 1 through 7. The figures show schematically illustrated embodiments and the pertinent potential profile on the electrodes according to the invention for each.

In the embodiments shown in Figures 1, 3, and 5 the sample is labelled 1, the beam path of the laser pulse 2, the laser light objective lens 3, the transit time path 4, and the downstream ion detector 5. The samples shown in Figures 1 and 5 are not transparent, so that laser light objective lens 3 must be located on the side of the solid surface to be studied. Sample 1 according to Figure 3 is transparent so that the laser light can be focussed through the sample, therefore on the sample side

opposite laser objective lens 3 and can cause the desired excitation of the sample material there.

In the embodiment according to Figure 1, path 4 is preceded by ion optics consisting of two tube sections 6 and 7. It is designed to suck the generated ions from the sample. Moreover, ion optics 8 pass only ions from a certain energy interval. Finally, ion optics 8 align the ion bundle in parallel so that after traversing drift route 4 it reaches ion detector 8. Between sample 1 and ion optics 8 is grating 9 which is used in the manner according to the invention to shape a time-defined ion pulse from the plasma which forms as a result of irradiation in the area of the sample surface. The potential profile on electrode 9 which is necessary in the case of analysis of positive ions is shown in Figure 2. At time 0, the instant of the laser pulse, there is positive potential  $U_1$  on electrode 9. The voltage value is selected such that positive ions cannot enter ion optics 8. For time interval  $(t_2 - t_1)$  electrode 9 has a negative potential ( $U_2$ ) so that positive ions can pass through grating 9. Afterwards electrode 9 again has potential  $U_1$  so that the "time window" is accurately defined and time blurring no longer occurs as a result of a longer lasting plasma. In the analysis of negative ions a corresponding potential profile homologous to the t-axis should be selected.

In the embodiment according to Figure 3 there are no ion optics. Transit time tube 4 is preceded by simply one extracting electrode 11. Between this extracting electrode 11 and transit time tube 4 there is deflection capacitor 12 with plates 13 and

14. With deflection plates of this type the same purposes, i.e., time-defined ion passage, can be achieved. If for example plate 14 is continually at ground or another certain potential, the ions are only passed when plate 12 has the same potential. As long as there are different potentials on these plates (compare Figure 4, the ground potential and potential  $U_3$ ), ions of the two polarities cannot reach transit time path 4. Under certain circumstances plate 14 can also be omitted.

Figure 5 shows one embodiment, again with ion optics 8 upstream of path 4. Between ion optics 8 and sample 1 are two grating electrodes 15 and 16 with time potential variations shown in Figures 6 and 7. Grating 15 is used again, as described for Figures 1 and 2, to suppress positive ions except for time interval  $(t_2 - t_1)$ . On grating 16, (compare Figure 7) except for time interval  $(t_2 - t_1)$ , there is continuously negative potential  $U_4$  with a magnitude selected such that electrons which can cause a signal background are retained.

In all Figures the "time windows" are given by difference  $(t_2 - t_1)$ . The time interval given by this time difference is preferably on the order of  $100 \times 10^{-9}$  seconds. By shifting or varying this time window the measurements can not only be optimized, but even studies on the mechanism of laser interaction can be done in addition.

## Laser microprobe

### Claims

1. Laser microprobe with a pulse laser for excitation of a sample and with a transit time mass spectrometer which comprises a path, characterized in that transit time path (4) is preceded by electrode system (9; 12 or 15, 16) for shaping a time-defined ion pulse from the plasma which is formed by sample excitation.

2. Laser microprobe according to claim 1, wherein there is grating electrode (9).

3. Laser microprobe according to claim 1, wherein there are one or two deflection plates (13, 14).

4. Laser microprobe according to claim 1, wherein there are two electrodes (15, 16), of which one is used to shape the ion pulse and the other to suppress electrons.

5. Laser microprobe according to claim 1, 2, 3, or 4, wherein there are ion optics between electrode system (9; 12 or 15, 16) and path (4).